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## BROMIC ACID

[7789–31–3]

Formula:  $\text{HBrO}_3$ ; MW 128.91

### Uses

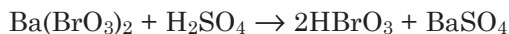
Bromic acid is used as an oxidizing agent; and also as intermediate in the preparation of dyes and pharmaceuticals.

### Physical Properties

Unstable compound; stable only in dilute aqueous solutions; solution turns yellow on standing; decomposes when heated to  $100^\circ\text{C}$ .

### Preparation

Bromic acid is prepared by adding sulfuric acid to barium bromate.



The product is distilled and absorbed in water. A 50% solution may be obtained by slow evaporation of the dilute solution in vacuum at  $-12^\circ\text{C}$ .

### Toxicity

Contact with skin and eyes can cause severe irritation.

## BROMINE

[7726–95–6]

Symbol Br; atomic number 35; atomic weight 79.904; a halogen group element; electron affinity 3.36359 eV; electronegativity 2.8; electron configuration  $[\text{Ar}] 3\text{d}^{10}4\text{s}^24\text{p}^5$ ; most stable valence states  $-1$  and  $+5$ , less stable valence states  $+1$  and  $+3$ ; a diatomic molecule ( $\text{Br}_2$ ) in liquid and vapor states over a wide range of temperature; two stable isotopes, Br-79 (50.57%) and Br-81 (49.43%).

### Occurrence and Uses

Bromine occurs in nature as bromide in many natural brine wells and salt deposits. It also is found in seawater at a concentration of 85 mg/L. The element was discovered by A. J. Balard and C. Lowig, independently in 1826. Bromine is used in bleaching fibers and as a disinfectant for water purification. Other applications are in organic synthesis as an oxidizing or brominating agent; in the manufacture of ethylene dibromide, methyl bromide and other bromo compounds for dyes and pharmaceutical uses; as a fire retardant for plastics; and in chemical analysis. Ethylene dibromide is used in anti-

knock fluids in motor fuels. Over 80% of the bromine produced is consumed in the manufacture of this compound.

### Physical Properties

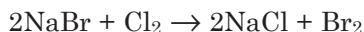
Dark reddish-brown liquid; the only nonmetallic element that is a liquid at ambient temperatures; strong disagreeable odor; volatilizes; density 3.12 g/mL at 20°C; vapor density 7.59 g/L; refractive index 1.6475; boils at 58.8°C; solidifies at -7.2°C; vapor pressure 64 torr at 0°C and 185 torr at 22°C; critical temperature 315°C; critical pressure 102 atm; critical volume 127 cm<sup>3</sup>/mol; surface tension 39.8 dynes/cm at 25°C; electrical resistivity 6.5 x 10<sup>10</sup> ohm-cm at 25°C; sparingly soluble in water (2.31 g/100g at 0°C and 3.35 g/100g at 25°C); soluble in common organic solvents.

### Thermochemical Properties

|                                       |                      |
|---------------------------------------|----------------------|
| $\Delta H_f^\circ$ (Br <sub>2</sub> ) | 0.0 kcal/mol         |
| $\Delta H_f^\circ$ (g)                | 26.74 kcal/mol       |
| $\Delta G_f^\circ$ (g)                | 19.69 kcal/mol       |
| $S^\circ$ (g)                         | 41.82 cal/degree mol |
| $C_p$ (g)                             | 4.97 cal/degree mol  |
| $C_p$ (l)                             | 8.56 cal/degree mol  |

### Production

Bromine is obtained from natural brines, salt beds and seawater. The bromide salts extracted from these sources are oxidized by chlorine to yield bromine:



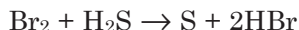
The bromine vapors are swept out into current of air or stream from the reaction chamber and trapped in an alkaline or reducing solution. Chlorine is removed over a stripping column. Bromine is purified in a fractionating column.

### Reactions

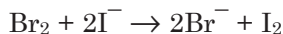
Most reactions of bromine are similar to other halogens. Its reactivity falls between chlorine and iodine. It readily attacks a number of metals including alkali and alkaline earth metals, palladium, platinum, aluminum, copper, antimony and tin, forming their bromides. These reactions can be vigorous to violent. It oxidizes a number of substances, including metal carbides, carbonyls, hydrides, and organic substances. It combines with hydrogen to form hydrogen bromide. Organic compounds, such as olefins, aromatics and alkanes undergo addition or substitution reactions yielding bromoderivatives. While the addition reaction with ethylene produces ethylene dibromide, bromination of benzene in the presence of iron as catalyst produces a substitution product, bromobenzene. Reaction with aqueous acetone and sodium chlorate at 40°C forms bromoacetone. Substitution reactions with alkanes yield alkyl bromides. Bromine combines with fluorine at room temperature

forming bromine trifluoride,  $\text{BrF}_3$ . The reaction produces luminous flame. Diluted with nitrogen, bromine vapor and fluorine react on heating at  $200^\circ\text{C}$  to form bromine trifluoride,  $\text{BrF}_3$ , or the pentafluoride,  $\text{BrF}_5$ . Reaction with iodine produces iodine monobromide,  $\text{IBr}$ .

Bromine reacts with phosphorus to form phosphorus tribromide,  $\text{PBr}_3$  or phosphorus pentabromide,  $\text{PBr}_5$ . The pentabromide forms in the presence of excess bromine. Bromine oxidizes hydrogen sulfide to sulfur:

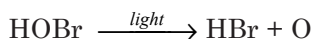
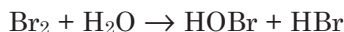


Bromine liberates iodine from iodide solution:



Combination reactions occur with several nonmetals. With sulfur, it forms sulfur monobromide,  $\text{S}_2\text{Br}_2$ . With the addition of selenium, products are selenium monobromide,  $\text{Se}_2\text{Br}_2$ , and selenium tetrabromide,  $\text{SeBr}_4$ . It yields unstable tellurium monobromide,  $\text{Te}_2\text{Br}_2$ , and a stable tetrabromide,  $\text{TeBr}_4$ , with tellurium.

In aqueous solution, bromine hydrolyzes slightly, forming unstable hypobromous acid,  $\text{HOBr}$ , which decomposes to hydrobromic acid and oxygen, causing the bleaching action of bromine water. The decomposition is accelerated by light.



Bromine water oxidizes aldose to lactones which hydrolyze to alfoinic acids.

Bromine combines with rubidium and cesium bromides forming solid polybromo complexes that can be crystallized from aqueous solutions. The complexes are soluble in liquid bromine.

Bromine reacts with cold nitric oxide forming nitrosyl bromide,  $\text{NOBr}$ , and nitrosyl tribromide,  $\text{NOBr}_3$ .

### Hazard

Most reactions of bromine are highly exothermic which can cause incandescence or sudden increase in pressure and rupture of reaction flasks. There are a number of cases of explosions documented in the literature. (NFPA. 1986. *Fire Protection Guide on Hazardous Materials*, 9th ed. Quincy, MA: National Fire Protection Association) Reactions of liquid bromine with most metals (or any metal in finely divided state), metal hydrides, carbonyls and nitrides can be explosive. Many oxides and halides of nonmetals, such as nitrogen triiodide or phosphorus trioxide, react explosively or burst into flame in contact with liquid bromine.

Bromine is moderately toxic by all routes of exposure. It is an irritant to the eye and respiratory tract. Inhalation can cause dizziness, headache, coughing

and lacrimation. A short exposure to 1,000 ppm for 15 minutes can be fatal to humans. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd edition. New York: John Wiley & Sons). Ingestion produces nausea, abdominal pain and diarrhea. The liquid is corrosive to skin.

## BROMINE PENTAFLUORIDE

[7789–30–2]

Formula:  $\text{BrF}_5$ ; MW 174.896

### Uses

Bromine pentafluoride is used as an oxidizer in liquid rocket propellants; and as a fluorinating agent in the processing of uranium.

### Physical Properties

Colorless to pale yellow liquid; fumes in air; density 2.466 g/mL at 25°C; boils at 40.8°C; decomposes above 460°C; solidifies at –60.5°C; reacts violently with water.

### Thermochemical Properties

|                                 |                     |
|---------------------------------|---------------------|
| $\Delta H_f^\circ$ (l)          | –109.6 kcal/mol     |
| $\Delta H_f^\circ$ (g)          | –102.5 kcal/mol     |
| $\Delta G_f^\circ$ (l)          | –84.1 kcal/mol      |
| $S^\circ$ (l)                   | 53.8 cal/degree mol |
| $S^\circ$ (g)                   | 76.5 cal/degree mol |
| $C_p$ (g)                       | 23.8 cal/degree mol |
| $\Delta H_{\text{fus}}$         | 1.355 kcal/mol      |
| $\Delta H_{\text{vap}}$ (at bp) | 7.31 kcal/mol       |

### Preparation

Bromine pentafluoride is prepared by fluorination of bromine at 200°C. The reaction is carried out in an iron or copper vessel. The halogens are diluted in nitrogen.

### Hazard

Bromine pentafluoride is a highly reactive compound combining explosively or with ignition with most elements and their compounds. Spontaneous explosion or flaming can occur when mixed with water, organic compounds, metal powder, metal halides, metal oxides, metal sulfides and chlorine (upon warming) (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley).

The liquid is dangerously corrosive to skin. The vapors are highly irritating to eyes, skin and mucous membranes.

## BROMINE TRIFLUORIDE

[7787-71-5]

Formula:  $\text{BrF}_3$ ; MW 136.90**Uses**

Bromine trifluoride is used as a fluorinating agent; and an electrolytic solvent for fluoride.

**Physical Properties**

Colorless liquid; hygroscopic; density 2.803 g/mL; boils at 125.8°C; solidifies at 8.8°C; vapor pressure 8 torr at 21°C; decomposes violently in water.

**Thermochemical Properties**

|                         |                      |
|-------------------------|----------------------|
| $\Delta H_f^\circ$ (l)  | -71.9 kcal/mol       |
| $\Delta H_f^\circ$ (g)  | -61.1 kcal/mol       |
| $\Delta G_f^\circ$ (l)  | -57.5 kcal/mol       |
| $\Delta G_f^\circ$ (g)  | -54.8 kcal/mol       |
| $S^\circ$ (l)           | 42.6 cal/degree mol  |
| $S^\circ$ (g)           | 69.9 cal/degree mol  |
| $C_p$ (l)               | 29.78 cal/degree mol |
| $C_p$ (g)               | 15.92 cal/degree mol |
| $\Delta H_{\text{vap}}$ | 11.37 kcal/mol       |

**Preparation**

Bromine trifluoride may be prepared by fluorination of bromine at 80°C. The halogen mixtures may be diluted in nitrogen or an inert gas.

**Hazard**

Bromine trifluoride is a highly reactive compound. It ignites or explodes in contact with a wide array of substances including water, finely divided metals, metal oxides and salts and organics. See Bromine Pentafluoride.

Skin contact with liquid can burn tissues. Vapors can damage eyes, lungs and respiratory tract.

## CADMIUM

[7440-43-9]

Symbol Cd; atomic number 48; atomic weight 112.41; a Group IIB (Group 12) metallic element; ionization potential 8.994eV; electron configuration  $[\text{Kr}]4d^{10}5s^2$ ; valence state +2; standard electrode potential,  $E^\circ$  -0.40V. The isotopes and their natural relative abundance are:

|        |        |
|--------|--------|
| Cd-106 | 1.25%  |
| Cd-108 | 0.89%  |
| Cd-110 | 12.49% |
| Cd-111 | 12.80% |
| Cd-112 | 24.13% |

|        |        |
|--------|--------|
| Cd-113 | 12.22% |
| Cd-114 | 28.73% |
| Cd-116 | 7.49%  |

### Occurrence and Uses

Cadmium was discovered by F. Stromeyer in 1817. In nature, it is mostly found in zinc deposits. The mineral, greenocktite (CdS) is found associated with the zinc ore, sphalerite (ZnS). Similarly zinc carbonate contains otavite (CdCO<sub>3</sub>) in small amounts. Its abundance in the earth's crust is estimated to be 0.15 mg/kg and in sea water 0.11 µg/L.

Cadmium is used for electroplating to impart a protective coating on iron and steel. It provides resistance against caustic alkalis. Another major application is in the nickel-cadmium storage battery where it enhances long service life and a wide operating range. Cadmium alloys find wide applications in bearing metals, solders, fusible metals, electrical conductors, power transmission wires, and jewelry. Cadmium electrodes are used in photoelectric cells, cadmium vapor lamps and selenium rectifiers. Graphite impregnated with cadmium is used in electrical controller switches, oil-less bearings and busing lines. Cadmium rods are used in nuclear reactors to absorb low-energy neutrons. Many cadmium compounds have a number of commercial applications.

### Physical Properties

Bluish-white lustrous soft metal; closed-packed hexagonal system; density 8.69 g/cm<sup>3</sup>; Brinell hardness 21; melts at 321.1°C; vaporizes at 767°C; vapor pressure 5 torr at 455°C; electrical resistivity 6.8 microhm-cm at 0°C; insoluble in water.

### Thermochemical Properties

|                                    |                                      |
|------------------------------------|--------------------------------------|
| $\Delta H_f^\circ$ (g)             | 26.72 kcal/mol                       |
| $S^\circ$ (s)                      | 12.38 cal/degree mol                 |
| $S^\circ$ (g)                      | 40.08 cal/degree mol                 |
| $C_p$ (s)                          | 6.21 cal/degree mol                  |
| $C_p$ (g)                          | 4.97 cal/degree mol                  |
| $\Delta H_{fus}$                   | 1.479 kcal/mol                       |
| $\Delta H_{vap}$                   | 23.87 kcal/mol                       |
| Co-eff. linear expansion (at 25°C) | $29.8 \times 10^{-6}/^\circ\text{C}$ |

### Production

Cadmium is obtained as a byproduct in zinc recovery processes. The metal volatilizes during roasting of zinc concentrates and collected as dust or fume in bag houses or electrostatic precipitators. The dusts are mixed with coal (or coke) and zinc chloride and calcined. The cadmium chloride formed volatilizes upon calcination and thus separates out from zinc. The chloride then is treated with sulfuric acid in the presence of an oxidizing agent. This converts lead, present as impurity in cadmium ore, to lead sulfate which precipitates out. Cadmium is finally separated from copper by the addition of zinc dust and

fractional precipitation.

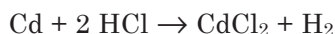
Cadmium also may be recovered from zinc ores and separated from other metals present as impurities by fractional distillation. Alternatively, the cadmium dust obtained from the roasting of zinc ore is mixed with sulfuric acid. Zinc dust is added in small quantities to precipitate out copper and other impurities. The metal impurities are removed by filtration. An excess amount of zinc dust is added to the solution. A spongy cadmium-rich precipitate is formed which may be oxidized and dissolved in dilute sulfuric acid. Cadmium sulfate solution is then electrolyzed using aluminum cathodes and lead anodes. The metal is deposited at the cathode, stripped out regularly, washed and melted in an iron retort in the presence of caustic soda, and drawn into desired shapes. More than half of the world's production of cadmium is obtained by electrolytic processes.

### Reactions

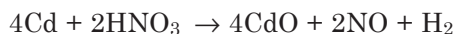
The metal is oxidized slowly in moist air at ordinary temperatures, forming a protective coating of cadmium oxide, CdO. At ordinary temperatures, it is not oxidized in dry air. However, upon heating it readily forms cadmium oxide.

The element combines with many nonmetals upon heating, forming its binary salts. It combines with halogens when heated, forming the corresponding halides. Heating with phosphorus, sulfur, and tellurium produces phosphide, Cd<sub>3</sub>P<sub>2</sub>; sulfide, CdS; and telluride, CdTe salts, respectively.

The metal is attacked by mineral acids. It reacts with warm dilute hydrochloric acid or sulfuric acid liberating hydrogen:



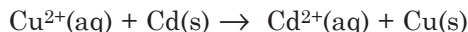
Reactions with hot dilute nitric acid give various oxides of nitrogen and hydrogen:



Aqueous solutions of alkali hydroxides do not attack cadmium. Cadmium replaces elements that are less electropositive in the activity series from their salt solutions. The standard electrode potential:



Thus, cadmium can displace a number of metals that are less active, such as copper, lead, silver, mercury, tin, and antimony from their aqueous salt solutions:





### Analysis

Cadmium in acidified aqueous solution may be analyzed at trace levels by various instrumental techniques such as flame and furnace atomic absorption, and ICP emission spectrophotometry. Cadmium in solid matrices is extracted into aqueous phase by digestion with nitric acid prior to analysis. A much lower detection level may be obtained by ICP–mass spectrometry. Other instrumental techniques to analyze this metal include neutron activation analysis and anodic stripping voltammetry. Cadmium also may be measured in aqueous matrices by colorimetry. Cadmium ions react with dithizone to form a pink-red color that can be extracted with chloroform. The absorbance of the solution is measured by a spectrophotometer and the concentration is determined from a standard calibration curve (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). The metal in the solid phase may be determined nondestructively by x-ray fluorescence or diffraction techniques.

### Toxicity

Cadmium is highly toxic to humans by both inhalation and ingestion. The acute poisoning effects are nausea, vomiting, diarrhea, headache, abdominal pain, muscular ache, salivation, and shock. In addition, inhalation of its dusts or fumes can cause cough, respiratory distress, congestion of lungs, and bronchopneumonia (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). The LD<sub>50</sub> (oral) in rat is in the range 250 mg/kg. The metal accumulates in the liver and kidneys, damaging these organs when exposure is chronic. Biological half-life in humans is estimated at 20–30 years (Manahan, S. 1989. *Toxicological Chemistry*. Chelsea, MI: Lewis Publishers). Cadmium is listed by the US EPA as one of the priority pollutant metals.

## CADMIUM ACETATE

[543–90–8]

Formula:  $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; MW 230.50; also, a dihydrate of the compound  $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  [5743–04–4] is known.

### Uses

Cadmium acetate is used for glazing ceramics and pottery; in electroplating baths; in dyeing and printing textiles; and as an analytical reagent for sulfur, selenium, and tellurium.

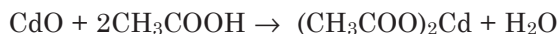
### Physical Properties

The anhydrous salt occurs as a colorless crystal while the dihydrate is a white crystalline solid; faint odor of acetic acid; density 2.34 g/cm<sup>3</sup> (dihydrate

2.01 g/cm<sup>3</sup>); melts at 255°C; dihydrate decomposes at 130°C; soluble in water and ethanol; pH of 0.2M aqueous solution 7.10.

### Preparation

Cadmium acetate is prepared by treating cadmium oxide with acetic acid:



Also, the compound may be prepared by treating cadmium nitrate with acetic anhydride.

### Analysis

Elemental composition: Cd 48.77%, C 20.84%, H 2.62%, O 27.77%. Aqueous solution may be analyzed for cadmium (see Cadmium) and the concentration of cadmium acetate can be estimated stoichiometrically.

## CADMIUM BROMIDE

[7789-42-6]

Formula:  $\text{CdBr}_2$ ; MW 272.22; also forms a tetrahydrate,  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  [13464-92-1]

### Uses

Cadmium bromide is used in lithography, engraving, and in the manufacture of photographic film.

### Physical Properties

White to yellowish powder or flakes; hexagonal crystal system; hygroscopic; density 5.192g/cm<sup>3</sup>; melts at 568°C; vaporizes at 844°C; soluble in water, alcohol, ether, acetone, and liquid ammonia.

### Thermochemical Properties

|                         |                      |
|-------------------------|----------------------|
| $\Delta H_f^\circ$      | -75.53 kcal/mol      |
| $\Delta G_f^\circ$      | -70.75 kcal/mol      |
| $S^\circ$               | 32.79 cal/degree mol |
| $C_p$                   | 18.33 cal/degree mol |
| $\Delta H_{\text{fus}}$ | 4.995 kcal/mol       |
| $\Delta H_{\text{vap}}$ | 27.49 kcal/mol       |

### Preparation

Cadmium bromide is prepared by heating cadmium with bromine vapor. Also the compound can be prepared by the treatment of dry cadmium acetate with glacial acetic acid and acetyl bromide. Alternatively, it may be obtained by dissolving cadmium or cadmium oxide in hydrobromic acid and evaporating the solution to dryness under helium in an inert atmosphere.

**Analysis**

Elemental composition: Cd 41.29%, Br 58.71%. The salt is dissolved in water and the aqueous solution is analyzed by AA or ICP spectrophotometry. The bromide anion in the aqueous solution may be measured by ion chromatography. Appropriate dilution may be needed for analysis

**CADMIUM CYANIDE**

[542–83–6]

Formula:  $\text{Cd}(\text{CN})_2$  ; MW 164.45

**Uses**

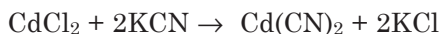
Cadmium cyanide is used as an electrolyte for electrodeposition of thin metallic cadmium coatings on metals to protect against corrosion.

**Physical Properties**

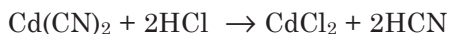
White, cubic crystal or powder; density 2.226 g/cm<sup>3</sup>; sparingly soluble in water 1.71g/100mL (at 15°C); slightly soluble in alcohol; dissolves in alkali, metal cyanides, and hydroxides.

**Preparation**

Cadmium cyanide may be prepared by treating a concentrated aqueous solution of cadmium chloride or cadmium nitrate with potassium cyanide or sodium cyanide. The white precipitate obtained is filtered, washed and dried.

**Reactions**

Cadmium cyanide reacts with dilute mineral acids, evolving hydrogen cyanide:



With organic acids, the reaction is slow. Reactions with sodium cyanide or potassium cyanide in aqueous solutions yield complex metal cyanide. For example, with potassium cyanide, the product is potassium tetracyanocadmate:

**Analysis**

Elemental composition: Cd 68.36%, C 14.61%, N 17.04%

Cadmium may be measured by various instrumental analysis (see cadmium). Cyanide may be extracted by distilling an acidified solution of cadmium cyanide and then purging the liberated hydrogen cyanide with air, passing it into a scrubbing solution of caustic soda. Cyanide in the scrubbing solution is

then measured by titration, or by colorimetry. In titrimetry, the distillate is titrated against silver nitrate standard solution using p-dimethylaminobenzalrhodamine indicator, while for colorimetric measurement, a color-forming reagent such as pyridine-barbituric acid or pyridine-pyrazolone may be used (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL: Lewis Publishers.

## CADMIUM CHLORIDE

[10108-64-2]

Formula:  $\text{CdCl}_2$ ; MW 183.306; also forms a hemipentahydrate.

### Uses

Cadmium chloride is used in metal finishing bath for cadmium plating. Also, it is used in photocopying, dyeing and printing.

### Physical Properties

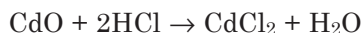
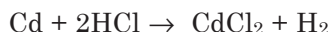
Colorless powder or crystal; hexagonal crystal system; hygroscopic; density  $4.047 \text{ g/cm}^3$ ; melts at  $560^\circ\text{C}$ ; vaporizes at  $960^\circ\text{C}$ ; highly soluble in water ( $140 \text{ g/100g}$  at  $20^\circ\text{C}$ ), also soluble in acetone; slightly soluble in alcohol; insoluble in ether.

### Thermochemical Properties

|                    |                                |
|--------------------|--------------------------------|
| $\Delta H_f^\circ$ | $-93.57 \text{ kcal/mol}$      |
| $\Delta G_f^\circ$ | $-82.21 \text{ kcal/mol}$      |
| $S^\circ$          | $27.55 \text{ cal/degree mol}$ |
| $C_p$              | $17.85 \text{ cal/degree mol}$ |

### Preparation

Cadmium chloride may be prepared by heating the metal with chlorine or hydrogen chloride gas. In the solution, it is formed by treating the metal or its salts, such as oxide, hydroxide, carbonate, or sulfide with hydrochloric acid:



The solution is evaporated and crystallized to yield a hydrated salt. The hydrated salt yields anhydrous cadmium chloride upon heating under hydrogen chloride or when refluxed with thionyl chloride.

Cadmium chloride also may be prepared by adding dry cadmium acetate to acetyl chloride in glacial acetic acid.

## CADMIUM CARBONATE

[513-78-0]

Formula:  $\text{CdCO}_3$ ; MW 172.41

### Uses

Cadmium carbonate occurs in nature as the mineral otavite. The commercial applications of this compound are limited. It is used as a catalyst in organic synthesis and as a starting material to prepare other cadmium salts.

### Physical Properties

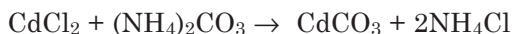
White powdery solid; density 4.258 g/cm<sup>3</sup>; decomposes on heating below 500°C; insoluble in water and liquid ammonia; soluble in acid (with reaction).

### Thermochemical Properties

|                    |                     |
|--------------------|---------------------|
| $\Delta H_f^\circ$ | -179.4 kcal/mol     |
| $\Delta G_f^\circ$ | -160.0 kcal/mol     |
| $S^\circ$          | 22.1 cal/degree mol |

### Preparation

Cadmium carbonate is precipitated by adding excess ammonium carbonate to a solution of cadmium chloride:



The precipitate is filtered and dried at 100°C. If an alkali metal carbonate is used instead of ammonium carbonate, a hydrated basic carbonate is obtained which upon heating with ammonium chloride at 150°C in the absence of air produces anhydrous carbonate.

Cadmium carbonate also may be obtained by slow absorption of cadmium oxide with carbon dioxide.

### Reactions

Cadmium carbonate decomposes to cadmium oxide and carbon dioxide at 357°C. The compound dissolves in mineral acids forming their cadmium salts and carbon dioxide:



Cadmium carbonate forms a cyanide complex ion,  $\text{Cd}(\text{CN})_4^{2+}$  in cyanide solutions. It dissolves in concentrated aqueous solutions of ammonium salts forming ammonium complexes.

### Analysis

Elemental composition: Cd 65.20%, C 6.97%, O 27.84%. See Cadmium.

## CADMIUM FLUORIDE

[7790-79-6]

Formula:  $\text{CdF}_2$ ; MW 150.41**Uses**

Cadmium fluoride is used in electronics and optics; to produce crystals for lasers; in the manufacture of phosphors and glass; in high temperature dry-film lubricants; and as a catalyst in organic reactions.

**Physical Properties**

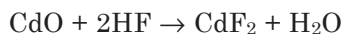
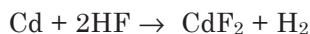
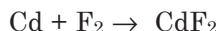
Colorless cubic crystal; density 6.33 g/cm<sup>3</sup>; melts at 1,110°C; vaporizes at 1,748°C; vapor pressure 5 torr at 1,231°C; moderately soluble in water, 4.35 g/100mL at 25°C; soluble in hydrofluoric and other mineral acids; practically insoluble in alcohol and liquid ammonia.

**Thermochemical Properties**

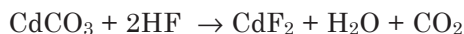
|                         |                     |
|-------------------------|---------------------|
| $\Delta H_f^\circ$      | -167.4 kcal/mol     |
| $\Delta G_f^\circ$      | -154.8 kcal/mol     |
| $S^\circ$               | 18.5 cal/degree mol |
| $\Delta H_{\text{fus}}$ | 5.4 kcal/mol        |
| $\Delta H_{\text{vap}}$ | 55.9 kcal/mol       |

**Preparation**

Cadmium fluoride is prepared by the reaction of gaseous fluorine or hydrogen fluoride with cadmium metal or its salt, such as chloride, oxide or sulfide:



It also may be obtained by dissolving cadmium carbonate in 40% hydrofluoric acid solution, evaporating the solution and drying in vacuum at 150°C:



It also may be prepared by mixing cadmium chloride and ammonium fluoride solutions, followed by crystallization.

**Analysis**

Elemental composition: Cd 74.74%, F 25.26%. The metal may be analyzed by various instrumental techniques (see Cadmium). Fluoride may be determined by ion chromatography or by using a fluoride ion-selective electrode.

## CADMIUM HYDROXIDE

[21041-95-2]

Formula:  $\text{Cd}(\text{OH})_2$ ; MW 146.43

### Uses

Cadmium hydroxide is used in storage battery anodes, in nickel-cadmium and silver-cadmium storage batteries, and in cadmium plating. It also is used to prepare other cadmium salts.

### Physical Properties

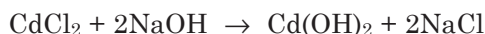
White powder or crystal; trigonal or hexagonal crystal system; density 4.79 g/cm<sup>3</sup>; decomposes slowly at 130°C; dehydration completes at 300°C; insoluble in water (2.6 mg/L at 20°C); soluble in dilute acids.

### Thermochemical Properties

|                    |                      |
|--------------------|----------------------|
| $\Delta H_f^\circ$ | -134.0 kcal/mol      |
| $\Delta G_f^\circ$ | -113.2 kcal/mol      |
| $S^\circ$          | 22.94 cal/degree mol |

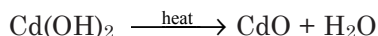
### Preparation

Cadmium hydroxide may be precipitated by adding any cadmium salt solution to a boiling solution of caustic soda or caustic potash:



### Reactions

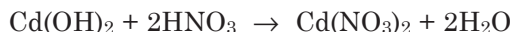
Cadmium hydroxide loses water on heating producing cadmium oxide:



Decomposition commences at 130°C and is complete at 300°C.

Cadmium hydroxide is more basic than zinc hydroxide. It forms anionic complex  $\text{Cd}(\text{OH})_4^{2-}$  when treated with concentrated caustic soda solution. It forms complexes with cyanide, thiocyanate and ammonium ions when added to the solutions of these ions.

Reactions with mineral acids produce their cadmium salts. With hydrochloric acid, sulfuric acid and nitric acid, the products are cadmium chloride, cadmium sulfate and cadmium nitrate, respectively:



Hydrated salts, such as  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $2\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ , crystallize upon evaporation.

**Analysis**

Elemental composition: Cd 76.77%, H 1.38%, O 21.85%. The compound may be identified non-destructively by x-ray techniques (see Cadmium).

**CADMIUM IODIDE**

[7790–80–9]

Formula:  $\text{CdI}_2$ ; MW 366.22

**Uses**

Cadmium iodide is used in lithography, process engraving, photography, electroplating, and in the manufacture of phosphors.

**Physical Properties**

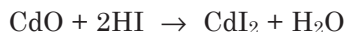
White, hexagonal flakes or crystals; slowly turns yellow upon exposure to air or light; occurs in two allotropic forms, the alpha and beta forms; density  $5.67 \text{ g/cm}^3$ ; melts at  $387^\circ\text{C}$  (alpha form) and  $404^\circ\text{C}$  (beta form); vaporizes at  $742^\circ\text{C}$ ; vapor pressures 1 and 5 torr at  $416$  and  $481^\circ\text{C}$ , respectively; soluble in water (86 g/100 mL at  $25^\circ\text{C}$ ), ethanol, acetone, ether, and ammonia.

**Thermochemical Properties**

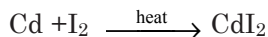
|                                  |                      |
|----------------------------------|----------------------|
| $\Delta H_f^\circ$ (alpha-)      | -48.59 kcal/mol      |
| $\Delta G_f^\circ$ (alpha-)      | -48.14 kcal/mol      |
| $S^\circ$ (alpha-)               | 38.50 cal/degree mol |
| $C_p$ (alpha-)                   | 19.12 cal/degree mol |
| $\Delta H_{\text{fus}}$ (alpha-) | 8.0 kcal/mol         |
| $\Delta H_{\text{vap}}$ (alpha-) | 25.33 kcal/mol       |

**Preparation**

Cadmium iodide is prepared by the addition of cadmium metal, or its oxide, hydroxide, nitrate or carbonate to hydriodic acid:



Also, the compound can be made by heating cadmium with iodine:

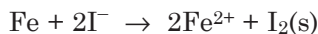


A brownish crystalline  $\beta$ -form of the salt may be obtained by slow crystallization from solutions or fused salt mixtures.

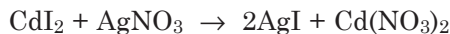
**Reactions**

In acid medium, cadmium iodide solution should exhibit the reduction reactions of  $\text{I}^-$  anion. Iodide anion is a fairly strong reducing agent which can reduce many metal ions in their higher oxidation states:

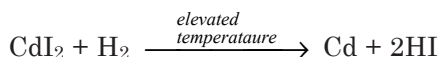




It undergoes double decomposition reactions in aqueous solution forming precipitates of insoluble products:



When heated with hydrogen, it is reduced to cadmium metal and hydrogen iodide:



### Analysis

Elemental composition: Cd 30.69%, I 69.31%. A small amount of salt is weighed accurately, dissolved in water, appropriately diluted, and analyzed by AA or ICP spectrophotometry. Iodide anion at similar trace concentrations may be analyzed by ion chromatography.  $\text{I}^-$  anion may be identified by adding a few drops of 6M  $\text{HNO}_3$  to a few drops of the aqueous solution of the salt, followed by the addition of 1mL 0.1 M  $\text{FeCl}_3$  solution and 1mL methylene chloride. A purple or pink bottom layer after shaking indicates the presence of iodide.

## CADMIUM NITRATE

[10325–94–7]

Formula:  $\text{Cd}(\text{NO}_3)_2$ ; MW 236.42; also forms a tetrahydrate,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$   
[10022–68–1]

### Uses

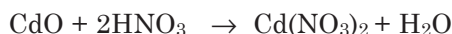
Cadmium nitrate is used for coloring glass and porcelain; (historically) as a flash powder in photography; and in the manufacture of many other cadmium salts.

### Physical Properties

White crystal or amorphous powder; hygroscopic; density 3.60 g/cm<sup>3</sup>; melts at 350°C; very soluble in water, also soluble in alcohols.

### Preparation

Cadmium nitrate is prepared by dissolving cadmium metal or its oxide, hydroxide, or carbonate, in nitric acid followed by crystallization:



### Reactions

Thermal dissociation at elevated temperatures produces cadmium oxide

and oxides of nitrogen. When hydrogen sulfide is passed through an acidified solution of cadmium nitrate, yellow cadmium sulfide is formed. A red modification of the sulfide is formed under boiling conditions.

When mixed with caustic soda solution, cadmium oxide forms precipitate of cadmium hydroxide. Many insoluble cadmium salts are obtained by such precipitation reactions. For example, mixing aqueous solutions of cadmium nitrate with ammonium tungstate results in precipitation of cadmium tungstate.

### Analysis

Elemental composition: Cd 47.55%, N 11.85%, O 40.60%. The metal may be analyzed in its acidified aqueous solution by various instrumental techniques (see Cadmium). Nitrate ion in the aqueous solution may be determined by ion chromatography or by using a nitrate ion-selective electrode.

### Toxicity

Cadmium nitrate is moderately toxic by ingestion, and possibly other routes of exposure.

LD<sub>50</sub> oral (rat): 300 mg/kg

The compound also is a confirmed human carcinogen.

## CADMIUM OXIDE

[1306–19–0]

Formula CdO; MW 128.41

### Uses

Cadmium oxide is used in storage battery electrodes. Its solution, mixed with sodium cyanide, is used in electroplating baths. Other uses are in PVC heat stabilizers; as an additive to nitrile rubbers and plastics to improve heat resistance; and in ceramic glazes and phosphors.

### Physical Properties

Occurs in two forms, alpha form—a colorless amorphous powder, and beta form—a reddish-brown crystal; density 6.95 g/cm<sup>3</sup> (alpha form) and 8.15 g/cm<sup>3</sup> (beta form); decomposes on rapid heating at 900°C; sublimation temperature 1,559°C; insoluble in water and alkalis; dissolves in mineral acids.

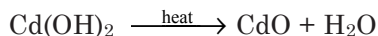
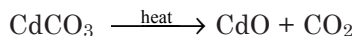
### Thermochemical Properties

|                    |                      |
|--------------------|----------------------|
| $\Delta H_f^\circ$ | –61.76 kcal/mol      |
| $\Delta G_f^\circ$ | –54.66 kcal/mol      |
| $S^\circ$          | 13.10 cal/degree mol |
| $C_p$              | 10.37 cal/degree mol |

### Preparation

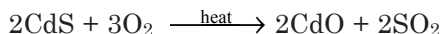
Cadmium oxide is prepared by the reaction of cadmium vapor with oxygen. The metal is first melted in a steel retort and transported into a heated chamber where it is vaporized. The vapor is reacted with air, and the cadmium oxide formed is collected in a bag house. The particle size of the product depends on the ratio of air to cadmium vapor. The oxide may be further purified and particles of uniform size may be obtained by calcination at low red heat.

Cadmium oxide also may be prepared by several other routes starting with various cadmium salts. The compound can be made by thermal decomposition of cadmium carbonate or cadmium hydroxide:

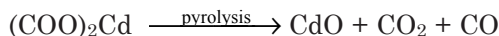
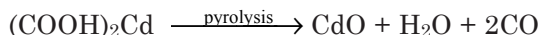


Similar thermal decomposition of cadmium nitrate or sulfate would yield the oxide.

Cadmium oxide also may be made by high temperature oxidation of cadmium sulfide:

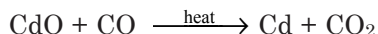
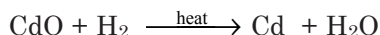


Finely divided oxide may be obtained by pyrolysis of cadmium salts of carboxylic acids, such as cadmium formate or oxalate:

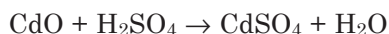
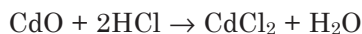


### Reactions

Reactions with reducing agents at elevated temperatures convert the oxide to metal:

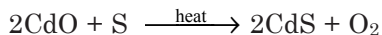


Cadmium oxide reacts with mineral acids forming their cadmium salts:



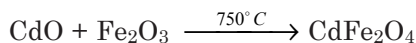
Similar reactions occur with carboxylic acids producing corresponding carboxylates of cadmium.

Heating a mixture of cadmium oxide and sulfur produces cadmium sulfide:



CdO slowly absorbs carbon dioxide forming cadmium carbonate,  $\text{CdCO}_3$ .

Reaction with amorphous silicon at  $900^\circ\text{C}$ , catalyzed by steam produces cadmium orthosilicate,  $\text{Cd}_2\text{SiO}_4$ . The same product also is obtained by reaction with silica. Finely divided oxide reacts with dimethyl sulfate forming cadmium sulfate. Cadmium oxide, upon rapid heating with oxides of many other metals, such as iron, molybdenum, tungsten, titanium, tantalum, niobium, antimony, and arsenic, forms mixed oxides. For example, rapid heating with ferric oxide at  $750^\circ\text{C}$  produces cadmium ferrite,  $\text{CdFe}_2\text{O}_4$ :



### Analysis

Elemental composition: Cd 87.54%, O 12.46%. CdO may be identified non-destructively by various x-ray techniques. Cadmium may be analyzed in aqueous phase by AA or ICP spectrophotometry following acid digestion. The oxide also can be analysed by various x-ray techniques.

## CADMIUM SULFATE

[10124–36–4]

Formula:  $\text{CdSO}_4$ ; MW 208.48; also forms two hydrates, cadmium sulfate monohydrate,  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  [7790–84–3] and cadmium sulfate octahydrate,  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  [15244–34–6].

### Uses

Cadmium sulfate is used as electrolyte in standard cells and electroplating baths. Also, it is used in pigments and fluorescent screens.

### Physical Properties

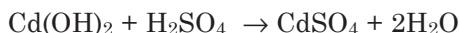
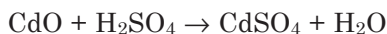
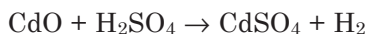
Colorless orthogonal crystal; the hydrates have monoclinic crystal system; density  $4.69 \text{ g/cm}^3$  (density of mono-, and octahydrates is  $3.79$  and  $3.08 \text{ g/cm}^3$ , respectively); melts at  $1,000^\circ\text{C}$  (octahydrate decomposes at  $40^\circ\text{C}$ ); soluble in water, insoluble in ethanol.

### Thermochemical Properties

|                    |                               |
|--------------------|-------------------------------|
| $\Delta H_f^\circ$ | $-223.1 \text{ kcal/mol}$     |
| $\Delta G_f^\circ$ | $-196.6 \text{ kcal/mol}$     |
| $S^\circ$          | $29.4 \text{ cal/degree mol}$ |
| $C_p$              | $23.8 \text{ cal/degree mol}$ |

**Preparation**

Cadmium sulfate is prepared by the reaction of cadmium metal or its oxide or hydroxide with dilute sulfuric acid:

**Analysis**

Elemental composition: Cd 53.92%, O 30.70%, S 15.38%.  $\text{CdSO}_4$  is dissolved in water and cadmium is analysed by atomic absorption or emission spectrophotometry, following appropriate dilution (see Cadmium). Sulfate ion in the solution may be determined by ion–chromatography or by gravimetry following treatment with barium chloride solution.

**CADMIUM SULFIDE**

[1306–23–6]

Formula:  $\text{CdS}$ ; MW 144.48

**Occurrence and Uses**

Cadmium sulfide occurs in nature as the mineral greenoktite. The compound is widely used in pigments for paints, baking enamels, ceramics and plastics. It imparts bright yellow to maroon, with strong retention of color and resistance to alkalis. It also is used in inks, phosphors, and fluorescent screens. Other applications of this compound are in photovoltaic and solar cells (for converting solar energy to electrical energy), photoconductors (in xerography), thin film transistors and diodes, rectifiers, scintillation counters, pyrotechnics, and smoke detectors.

**Physical Properties**

Yellow to orange crystal; occurs as two polymorphs, hexagonal alpha form and cubic beta form; exhibits stable wurtzite structure at lower temperature, and zinc blende type structure at higher temperatures; the beta form converts to alpha form when heated at 750°C in sulfur atmosphere; sublimes at 980°C; practically insoluble in water (1.3 mg/L at 20°C);  $K_{\text{sp}}$   $3.6 \times 10^{-29}$ ; dissolves in dilute mineral acids on heating or concentrated acids at ordinary temperatures (decomposes with liberation of  $\text{H}_2\text{S}$ ).

**Thermochemical Properties**

|                    |                      |
|--------------------|----------------------|
| $\Delta H_f^\circ$ | -38.70 kcal/mol      |
| $\Delta G_f^\circ$ | -37.40 kcal/mol      |
| $S^\circ$          | 15.51 cal/degree mol |

**Preparation**

Cadmium sulfide may be prepared by precipitation from an aqueous solution of its soluble salts such as cadmium chloride or cadmium nitrate by passing hydrogen sulfide. The reactions may be carried out in acidic, neutral or alkaline solutions using various cadmium salts to obtain different crystal modifications as shown in the table below.

| Reaction of H <sub>2</sub> S with Cadmium Salts under Varying Conditions |                                  |                |
|--------------------------------------------------------------------------|----------------------------------|----------------|
| Aqueous Solution of Cd Salt                                              | Reaction Conditions              | CdS Color      |
| CdCl <sub>2</sub>                                                        | neutral pH; ordinary temperature | yellow crystal |
| CdCl <sub>2</sub>                                                        | acidic pH; boiling solution      | red crystal    |
| Cd(NO <sub>3</sub> ) <sub>2</sub>                                        | neutral pH; ordinary temperature | yellow crystal |
| Cd(NO <sub>3</sub> ) <sub>2</sub>                                        | acidic pH; boiling solution      | red crystal    |
| CdSO <sub>4</sub>                                                        | neutral pH; ordinary temperature | yellow crystal |
| CdSO <sub>4</sub>                                                        | acidic pH, boiling solution      | red crystal,   |
| Cd(C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub>           | acidic pH; ordinary temperature  | yellow crystal |
| Cd(C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub>           | alkaline ammoniacal solution     | red solution   |
| Cd(ClO <sub>4</sub> ) <sub>2</sub>                                       | acidic pH; warm solution         | yellow crystal |

Cadmium sulfide also may be obtained by treatment of sodium or other alkali metal sulfide solution with that of a soluble cadmium salt. The compound also may be prepared by heating a mixture of cadmium or its oxide with sulfur at 800°C; or by the reaction of H<sub>2</sub>S with cadmium vapor at 800°C.

**Analysis**

Elemental composition: Cd 77.81%, S 22.91%. In crystalline state, it may be identified by x-ray diffraction measurement. In aqueous acid extract following digestion with nitric acid, cadmium may be measured by various instrumental techniques. (see Cadmium). Warming with dilute mineral acids liberates H<sub>2</sub>S, which may be identified by its odor or by browning of a white paper soaked in lead acetate solution.

**Toxicity**

Cadmium sulfide is moderately toxic to experimental animals by all routes of exposure. Toxicity in humans is low. It is, however, carcinogenic to humans.